Synthesis of Alcohols Higher than Methanol from Carbon Monoxide and Hydrogen[1]

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IN ADDITION to the methanol process previously described[2] several methods have been suggested lately for high-pressure synthesis of mixtures of aliphatic alcohols from carbon monoxide and hydrogen. These processes are all more or less alike in so far as the experimental conditions are concerned, the main difference lying in the type of catalysts and the temperatures employed in carrying out the synthesis. While in the methanol process this one alcohol is the main product of reaction, a variety of aliphatic alcohols, ranging from methanol and up, result from the other processes. Obviously, the products chiefly sought are the alcohols higher than methanol and ethanol.

A German patent[3] mentions the formation of a number of oxygenated organic compounds, including alcohols, by reactions at high pressure of carbon monoxide and hydrogen. The catalysts suggested are mixtures of metallic oxides, preferably with an addition of hydroxides of the alkali metals. In trying to duplicate one of the samples quoted in this patent, Fischer found that nothing but water resulted, while when iron was added to the contact mass alcohols and other oxygenated compounds were formed. Fischer then worked out his so-called "synthol" process using an iron-alkali catalyst.[4] The complex mixture of liquid products obtained by this method contains a considerable amount of aliphatic alcohols. Apparently, the total amount of higher alcohols equals or slightly exceeds the sum of methanol and ethanol present.

Some of the patents relating to the manufacture of higher alcohols[5] specify the use of hydroxides of the alkali and alkali-earth metals or the carbonates of the alkali metals, in connection with what may be called typical methanol catalysts. Two other patents[6] claim the production of higher alcohols employing the same type of catalysts, the effect of temperature and rate of gas flow being particularly emphasized.

Starting with carbon monoxide and hydrogen, the free-energy decrease is larger the higher the alcohol formed. This holds true whether water or carbon dioxide is liberated by the reaction according to the general equations:

$$n\mathrm{CO} + 2n\mathrm{H_2} = \mathrm{C}n\mathrm{H_{2n-1}OH} + (n-1)\mathrm{H_2O_{(gas)}} \quad (1)$$

$$(2n-1)\mathrm{CO} + (n+1)\mathrm{H_2} = \mathrm{C}n\mathrm{H_{2n-1}OH} + (n-1)\mathrm{CO_2} \quad (2)$$

Using the free-energy value —44,000 calories for the formation of the lower aliphatic alcohols from the elements[7]—one obtains the following free-energy quantities:

Alcohol	Free-Energy Decrease per Carbon Atom, $F_{298}°$ A. Reaction (1)	Reaction (2)
	Calories	*Calories*
CH_3OH	−10,920	−10,920
C_2H_5OH	−16,744	−13,577
C_3H_7OH	−18,495	−13,994

These values show that the tendency for the reactions to go increases with increasing molecular weight of the aliphatic alcohols, and the problem therefore becomes one of searching for the most suitable catalysts. No matter what the reaction is the volume always decreases in the ratio 3:1. As for the methanol reaction,[2] pressure is required in order to secure reasonable quantities of alcohol and depress side reactions.

The present paper describes experiments made with different types of catalysts in order to study the formation of higher alcohols in accordance with the processes outlined above.

Experimental Work

On account of the difference between the products of reaction, the investigation can most suitably be divided into two separate parts comprising experiments concerned with (A) iron-alkali catalysts, and (B) metallic oxide catalysts. The raw materials were in both cases carbon monoxide and hydrogen, and the reactions were carried out under high pressure at elevated temperature. The apparatus used was the same as that described in the paper on the methanol process.[2]

(A) EXPERIMENTS WITH CATALYSTS OF THE IRON-ALKALI TYPE

Preliminary experiments demonstrated that it was possible to reproduce Fischer's results using as the catalyst iron or steel turnings impregnated with potassium hydroxide. Characteristic of this process is the formation of a liquid product consisting of an aqueous and an oily layer. As shown by Fischer's analyses,[4] the aqueous layer contains in addition to water, lower alcohols, particularly methanol and ethanol, acids, aldehydes, and ketones, while the oily layer chiefly consists of higher alcohols and hydrocarbons. From ultimate analyses of the two layers and of the exit gas it was possible to calculate the efficiency of the process for each run —i. e., the amount of entering carbon monoxide converted into the various products of reaction.

Usually 40 cc. of catalyst were employed with an exit gas flow of 16 to 80 liters per hour, at standard conditions of temperature and pressure (0° C. and 760 mm.), corresponding to space velocities within the range of 400 to 2000 cc. of gas per hour per cc. of catalyst. A larger volume of catalyst mass (120 cc.) was occasionally used in order to permit production of larger amounts of liquid per unit time for the same space velocities. Unless otherwise stated the pressure was 3000 pounds per square inch (204 atmospheres) with a gas mixture consisting of approximately 25 per cent carbon monoxide and 75 per cent hydrogen.

General Catalyst Study

Using a catalyst composed of cast-iron turnings impregnated with potassium hydroxide (run 136A), the yield of water-soluble products was low and only a trace of oil was obtained at 400–416° C. The liquid obtained consisted mainly of water with traces of methanol and about 1 per cent of aldehyde.

With 0.83 per cent carbon steel impregnated with potassium hydroxide and alumina (run 145C) fair yields were obtained at 411° C. An oily product representing 5.5 per cent of the

[1] Received January 18, 1928.

[2] Lewis and Frolich, *Ind. Eng. Chem.*, **20**, 285 (1928).

[3] German Patent 293,787 (March 8, 1913); U. S. Patent 1,201,850 (October 17, 1916).

[4] "Conversion of Coal into Oils," (1925); *Ind. Eng. Chem.*, **17**, 574 (1925).

[5] U. S. Patent 1,201,850 (October 17, 1916); French Patent 581,816 (May 19, 1924).

[6] British Patents 238,319 (August 20, 1925); 240,955 (1925).

[7] Parks, *J. Am. Chem. Soc.*, **47**, 338 (1925).

entering carbon monoxide and an aqueous layer containing water and water-soluble products, corresponding to 45 per cent of the entering carbon monoxide, were produced. Gaseous products, mainly carbon dioxide and methane, amounted to 40.8 per cent.

In one run (148D) a good methanol catalyst was placed in the chamber above the iron-alkali-alumina catalyst used in the previous run. With this arrangement the gas passed through the methanol catalyst before reaching the iron-alkali-alumina catalyst. At 310° C. the carbon monoxide converted into aqueous products was 63.9 per cent. No oily products were formed. As the temperature increased an oily layer appeared, and at 414° C. an 8 per cent conversion to oil was obtained along with a 22 per cent conversion into aqueous compounds. When the 8 per cent oil was obtained, however, 61.2 per cent of the entering carbon monoxide was consumed in the formation of methane, ethane, carbon dioxide, and unsaturated hydrocarbons. At 353° C. the operation was more efficient. The oil yield was 5.4 per cent and the yield of water-soluble compounds 39.5 per cent, while 48.4 per cent of the entering carbon monoxide went to gaseous products.

An intermittent run of 20 hours was made with a steel potassium hydroxide catalyst at an average temperature of 427° C. (run 149C) in order to synthesize sufficient oil for a boiling-range determination. Of the entering carbon monoxide 11.8 per cent was converted to oily products, 10.1 per cent to water-soluble compounds, and 68 per cent to gaseous products. The ultimate analysis of the oily product of this run showed carbon 52 per cent, hydrogen 13 per cent, and oxygen 35 per cent, which corresponds approximately to C_2H_6O. The boiling range is given in Table VII. The low-boiling fractions were colorless, but as the boiling point increased the liquid became yellow and had a pale straw color in the 179.0–209.0° C. fraction. The residue was a brown, viscous liquid.

A catalyst composed of 12 per cent chromium-steel turnings impregnated with potassium hydroxide was found to be active at moderately low temperatures, giving fair oil yields at 300–330° C. (run 168B). The yield of oil from this experiment was 13.4 per cent at 334° C.; 3.4 per cent of the carbon moxonide was converted into aqueous products and 56.7 per cent to gaseous products.

Section 1 of Table IV briefly summarizes the results of the foregoing experiments under conditions of maximum oil yield.

In all cases oil production seems to be accompanied by a considerable loss of carbon monoxide in side reactions. Apparently this is because the higher temperature favors the reactions $CO + 3H_2 = CH_4 + H_2O$ and $2CO + 2H_2 = CO_2 + CH_4$.

Fischer claims that below 380° C. the reaction proceeds at a very low rate while above 460° C. there is an increasing tendency to deposit carbon. Between these limits the reaction velocity increases with rising temperatures until a maximum of oil is obtained which is conditioned by its equilibrium with other constituents in the gas. If the temperature is lower more alcohol and less oil are produced; if higher, more oil will be formed, while the alcohol in the aqueous liquid is diminished. Under the conditions employed by Fischer, the best results were realized at 410° C., provided the rate of gas flow was adjusted to secure the establishment of equilibrium. From this it would seem that a novel result was obtained in run 168B (Table IV), in which a comparatively large ratio of oil to aqueous products was obtained at 334° C. using a 12 per cent chromium steel–alkali catalyst. A rather detailed study was therefore made of the effect of variations of the chromium content of the catalyst.

The synthesis of alcohols higher than methanol from carbon monoxide and hydrogen under high pressure has been studied for two distinctly different types of catalysts—(1) iron impregnated with alkali, and (2) mixtures of metallic oxides.

Particularly the composition of the iron-alkali catalyst has been varied within wide limits. In general, the results obtained with this type of catalyst show that it is very difficult to suppress side reactions leading to the formation of carbon dioxide, methane, water, and elementary carbon. The liquid product usually separates in two layers—one containing water in predominating quantities, the other being of oily character and consisting of complex mixtures of the simpler oxygenated aliphatic compounds as well as hydrocarbons of varying boiling point.

When operated at sufficiently high temperatures, catalysts composed of mixtures of metallic oxides give considerable amounts of higher alcohols in addition to methanol, water, and gaseous by-products.

For both types of catalysts the percentage of carbon monoxide lost in undesirable side reactions is quite serious, and in this respect the iron-alkali catalysts are inferior to the oxide mixtures.

Variation of Chromium Content of Chromium Steel–Potassium Hydroxide Catalyst

A list of the various catalysts containing iron and chromium is given in Table I. In testing these catalysts the experimental conditions were, in general: pressure 3000 pounds per square inch (204 atmospheres), temperature between 300° and 450° C., and an exit rate of gas flow of approximately 50 liters per hour with an entering gas containing about 25 per cent of carbon monoxide and 75 per cent hydrogen, the volume of the catalyst being 40 cc.

As a whole the results were decidedly unsatisfactory. Either no reaction or only very slight activity was observed in every case except with catalyst II–30–1 (2.75 per cent chromium steel). In section 2 of Table IV the yields previously obtained with a catalyst containing 12 to 14 per cent chromium steel (II–16–2) are compared with the results from this experiment. The reduction of the chromium content of the steel from 12–14 per cent to 2.75 per cent, with an accompanying increase in the carbon content from 0.35 per cent to 0.9 per cent, has not materially changed the yield of aqueous and oily products, but it has decreased the yield of gaseous products from 56.7 per cent to 38.5 per cent.

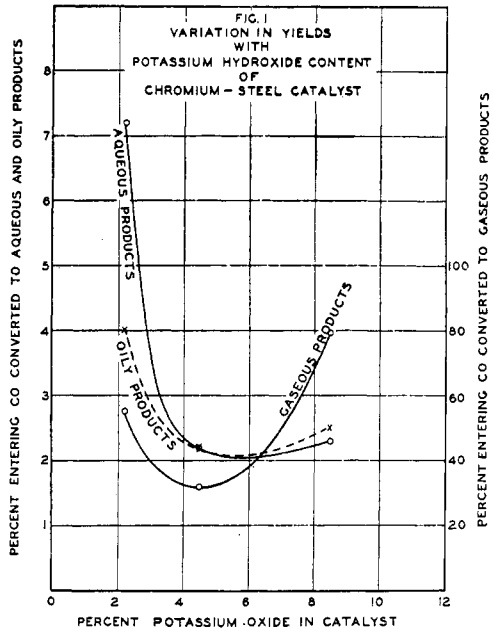
Table I—Catalysts Containing Chromium and Iron

Run	Catalyst	Catalyst Composition	Per cent
173 A, B, C	II–19–1	Powdered metallic chromium	95.5
		Potassium oxide	4.5
174 A, B, C	II–21–2	Powdered metallic chromium	88.4
		Electrolytic iron	7.1
		Potassium oxide	4.5
184	II–23–1	28% Chromium-iron alloy (no carbon)	95.5
		Potassium oxide	4.5
211	II–27–1	Ferrochrome (65–70% Cr, 6.0% C)	95.5
		Potassium oxide	4.5
213	II–28–1	Ferrochrome (65–70% Cr, 0.3% C)	95.5
		Potassium oxide	4.5
214	II–29–1	Chromium metal (95.9% Cr, 0.47% C)	95.5
		Potassium oxide	4.5
217	II–30–1	Chromium steel (2.75% Cr, 0.9% C)	95.5
		Potassium oxide	4.5
220	II–31–1	Ferrochrome (annealed) (65–70% Cr, 0.3% C)	95.5
		Potassium oxide	4.5

In view of these data and the negative results with alloys of high chromium content (Table I), it seems that a low-chromium steel offers the best possibilities of efficient oil formation. It should be pointed out, however, that the increase in the carbon content of the steel may also be responsible for the decrease in the formation of gaseous products, since advantages are claimed for the use of catalysts containing carbon.[8]

Variation in Potassium Hydroxide Content of Chromium Steel–Potassium Hydroxide Catalyst

In order to determine the effect of the potassium hydroxide content on the activity of the chromium steel–potassium hydroxide catalyst, three runs were made with catalysts of the compositions given in Table II. The experimental conditions under which this comparison was made were: temperature about 330° C., entering gas flow of 20 to 25 liters per hour, and pressure 3000 pounds per square inch (204 atmospheres) with an entering gas containing 40 per cent carbon monoxide. The results are shown in section 3 of Table IV.



The best yields were obtained with the catalyst (II–25–1) containing the smallest amount of potassium hydroxide (2.2 per cent potassium oxide). There is apparently little difference in the aqueous and oily yield with 4.5 per cent and 8.5 per cent potassium oxide, but a considerable change, from 31.6 per cent to 79.4 per cent, is observed in the conversion of carbon monoxide to gaseous products. (Figure 1)

Variation of Carbon Monoxide Content of Gas with a Chromium Steel–Potassium Hydroxide Catalyst

Several experiments were made to determine the effect of the carbon monoxide concentration in the gas on the yields of the various products. In section 4 of Table IV the results of these experiments are summarized and compared with the yields obtained in run 168B. The experimental conditions were the same as those outlined above, except that the entering rate of flow was 50 to 55 liters per hour. A catalyst containing 4.5 per cent potassium oxide (II–16–4, Table II) was used throughout.

These data show that the best yields are obtained with a gas mixture low in carbon monoxide (Figure 2). It is of interest also to note that in a run (210A) where a flow of 23.2 liters per hour was used with a gas containing 67.1 per cent carbon monoxide, 15.8 per cent conversion to oily products was obtained along with 48.8 per cent conversion to gaseous products. However, in this experiment very heavy carbon deposition took place in the chamber. This observation confirms Fischer's conclusion that high carbon monoxide concentrations give increased oil yields but also cause carbon deposition.

[8] German Patent 295,203 (June 23, 1914).

Table II—Chromium-Steel Catalysts with Various Amounts of Potassium Hydroxide

Run	Catalyst	Catalyst Composition	Per cent
192	II–24–1	12–14% Chromium-steel turnings	91.5
		Potassium oxide (as KOH)	8.5
195 A, B	II–25–1	12–14% Chromium-steel turnings	97.8
		Potassium oxide (as KOH)	2.2
199	II–16–4	12–14% Chromium-steel turnings	95.5
		Potassium oxide (as KOH)	4.5

Effect of Combining a Hydration Catalyst with an Iron-Alkali Catalyst

It was observed that the exit gases, in experiments with iron-alkali catalysts, would contain up to 4 or 5 per cent of unsaturated hydrocarbons. A run (207) was therefore made with alumina in the lower part of the chamber in an attempt to hydrate the unsaturateds with the production of alcohols. An iron-alkali catalyst (II–16–5, 12 to 14 per cent chromium steel) was placed in the normal position in the middle of the chamber. The gases, after leaving this catalyst, passed through the alumina in the lower and cooler portion of the chamber before going to the condenser. In Table III the results of this experiment (207) are compared with those obtained with the corresponding iron-alkali catalyst alone (168B).

Table III—Data for Iron-Alkali Catalysts

Run 207: Iron-alkali catalyst + alumina
Run 168B: Iron-alkali catalyst alone

Run	Inlet Gas				Exit Gas				
	CO_2	CO	H_2	CH_4	CO_2	CO	Unsatd.	H_2	CH_4
	%	%	%	%	%	%	%	%	%
207	0.0	21.1	72.4	2.2	7.0	3.1	2.1	68.7	15.3
168B	0.2	24.7	69.5	4.5	5.7	8.7	1.7	62.9	20.2

Run	Rate of Gas Flow	Temperature	Entering CO Converted to: Aqueous products	Oily products	Gaseous products
	Liters/hour	° C.	%	%	%
207	46.5	332	3.5	17.1	68.5
168B	54.3	334	3.4	13.4	56.7

From these data it appears that the alumina has increased the yield of both oily and gaseous products, although the amount of unsaturated hydrocarbons is slightly increased in the exit gas. The increased losses as gaseous products more than offset the gain in oily products, so that no advantage is gained by combining the two catalysts. It was observed at the end of the experiment that the alumina, which was granular when placed in the chamber, was in the form of a putty saturated with oil.

Tests of Miscellaneous Catalysts

A large number of catalysts of widely varying composition and including an active ammonia catalyst of the iron-alkali type, obtained by courtesy of the Fixed Nitrogen Laboratory, Washington, D. C., were also tried out. The results, which are not particularly promising, may be summarized thus: There is practically no activity with catalysts containing iron oxide and potassium hydroxide. Nickel steel (10 per cent) seems to be rather violent in its action, since particles of carbon were observed in the product; no oils were formed, however.

Table IV—Data of Experiments with Iron-Alkali Catalysts

Run	Catalyst	CO in Entering Gas %	Exit Gas Flow *Liters/hour*[a]	Temp. ° C.	Pressure *Atmos.*	Entering Carbon Monoxide Converted to: Aqueous products %	Oily products %	Gaseous products %
				SECTION 1				
136A	II-3-1	20.8	26.8	400	283	12.5	Trace	71.8
145C	II-5-1	25.8	118.0	411	207	45.0	5.5	40.8
148D	II-5-2	21.6	30.5	414	204	22.0	8.0	61.2
149C	II-6-1	25.2	44.6	395	204	10.1	11.8	68.8
168B	II-16-2	24.7	49.6	334	204	3.4	13.4	56.7
				SECTION 2				
168B	II-16-2	24.7	49.6	334	204	3.4	13.4	56.7
217	II-30-1	30.6	42.5	337	204	2.2	13.0	38.5
				SECTION 3				
192	II-24-1	39.8	20.9	333	204	2.3	2.5	79.4
195B	II-25-1	39.8	17.0	326	204	7.2	4.0	55.0
199	II-16-4	40.0	23.1	334	192	2.2	2.2	31.6
				SECTION 4				
168B	II-16-2	24.7	49.6	334	204	3.4	13.4	56.7
189B	II-16-3	39.6	50.5	337	201	3.0	3.3	34.8
210B	II-16-5	67.1	46.1	339	205	0.0	8.5	40.0
				SECTION 5				
178D	I-51-1 over	23.1	18.2	325	207	40.3		37.0
178E	II-16-2	23.1	78.1	327	204	39.6		19.6
				SECTION 6				
182	I-51-1 over	23.1	23.2	326	204	62.0		25.5
183	II-16-1	23.1	20.5	327	204	41.5		32.2

[a] Normal temperature and pressure.

Experiments with a Methanol Catalyst Followed by an Iron-Alkali Catalyst

Several experiments were made by first converting a portion of the entering gas mixtures to methanol and then passing the methanol-carbon monoxide-hydrogen mixture through an iron-alkali-higher alcohol catalyst. A good methanol catalyst (zinc-chromium, I-51-1) was used and operated at 283° and 325° C. The entering rate of gas flow was 80 liters per hour at the lower temperature and both 20 and 80 (approximately) liters per hour at the higher temperature. Considerable liquid was formed in all runs, but only at 325° C. did a few drops of oily product appear. Runs 178D and 178E were made at 325° C., the former with an inlet rate of 30 liters and the latter with 80 liters per hour. The yields in both runs, based on ultimate analyses of the products, are shown in section 5 of Table IV. It was noticed that the lower rate of flow produced more oil than the higher, although the actual amounts were small. From the table it is seen that this higher oil formation corresponds to a higher percentage of entering carbon monoxide being converted to gaseous products, while the percentage of carbon monoxide converted to total liquid products is about the same for both runs. Higher alcohols were detected by fractionation of both products but not identified.

Since fair efficiencies were obtained with considerably smaller losses than shown by an iron-alkali catalyst alone, two additional runs of about 24 hours' duration were made in order to obtain sufficient product for more complete examination. The experimental conditions of the two long runs (182 and 183) were similar to those of run 178D, except that in run 183 the period of reduction of the catalyst was 3 1/2 hours instead of the usual 1 3/4 hours at 10 atmospheres and 150° C. As shown in section 6 of Table IV, considerable difference was found between the efficiencies of conversion in the two runs. Only a few drops of oily product appeared in each case. Fractionations disclosed higher alcohols while methanol was present in predominating quantities. The product from run 182 contained about 75 per cent methanol, while 183 was lower in methanol (45 per cent) but contained a larger quantity of higher alcohols.

(B) EXPERIMENTS WITH METALLIC OXIDE CATALYSTS

Extensive preliminary experiments demonstrated that temperature entered as a most important variable when catalysts composed of metallic oxides were employed. Thus, higher alcohols did not form unless temperatures around 450° to 500° C. were reached, which is considerably higher than the 300° to 350° C. required for methanol formation.

The following catalysts were made up:

I-48-1 was prepared by dissolving pure zinc oxide in molten potassium dichromate. The mass was then cooled and crushed.

I-39-1 was prepared by mixing intimately 8 parts zinc oxide, 10 parts chromium trioxide, and 8 parts of barium hydroxide. Copper was used as a supporting medium.

I-47-1 was made from zinc oxide, ammonium dichromate, and potassium carbonate. After mixing, the materials were dried in an oven to remove the ammonia.

I-70-1 consisted of barium carbonate and copper hydroxide on a copper support. The barium carbonate amounted to only 0.5 per cent of the total catalyst.

The results of experiments made with these catalysts are listed in Table V. As an example of the type of products formed, we may consider the liquid products from runs 278A and B, which were combined in order to obtain a large sample for fractionation. In determining the constituents of the different fractions three separate means were employed—

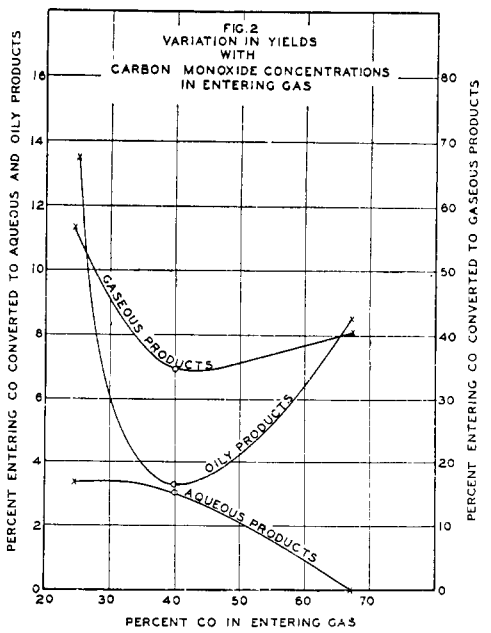


Table V—Higher Alcohol Formation from Carbon Monoxide and Hydrogen—Oxide Catalyst (40 cc.)

(Composition of entering gas mixture: 25.9% CO, 69.0% H_2, 4.1% CH_4)

Run	Catalyst	Temp.	Pressure	Exit Gas	Liquid	Ratio Oil to Aqueous Layer	Analysis of Exit Gas					Remarks
							CO_2	CO	H_2	CH_4	C_2H_6	
		° C.	*Atmos.*	*Liters/-hour*[a]	*Cc./hour*		%	%	%	%	%	
275A	I-48-1	370 550	225	37.8	2.9	0.10	7.0	8.8	72.0	...	...	Trace of oil at 445° C.
275B	I-48-1	483	245	40.2	2.8	1.0	4.1	8.8	75.8	6.7	1.0	Oil at 468° C.
276	I-39-1	291 490	245	34.0	1.2	Traces of oil	3.4	9.6	...	...	...	Fractionation showed 23 per cent methanol by volume
278A	I-47-1	460	242	45.3	3.5	1.26	...	...	...	...	...	Oil appeared at 470° C.
278B	I-47-1	490	238	65.8	4.9	1.64	3.6	15.2	...	...	...	Oil appeared at 470° C.
280	I-70-1	253 490	222	40.4	5.2	0.15	...	...	...	...	...	Oil appeared between 450° to 490° C.

[a] Normal temperature and pressure.

boiling point, refractive index, and derivatives. Table VI shows the composition of the total liquid product, including both the oily and the aqueous layers.

Table VI—Composition of Total Liquid Product in Runs 278A and B

Constituent (Anhydrous)	Oily Layer	Aqueous Layer	Total
	%[b]	%[b]	%
Methanol	11.4	6.4	17.8
Ethanol	Trace	2.3	2.3
Propanols	23.9	9.5	33.4
Butanols[a]	2.5	...	2.5
Amyl alcohols[a]	9.0	...	9.0
Higher alcohols	Small amount	...	Small amount
Water	13.8	21.8	35.6

[a] The individual figures for butanols and amyl alcohols are somewhat uncertain, while the total percentage should be nearly correct.
[b] Per cent by volume.

The total yield of alcohols from these runs based on the entering carbon monoxide was 13.9 per cent, and the waste amounted to 34.1 per cent. The total yield of alcohols other than methanol was 11.3 per cent. Normal propanol was the most important organic constituent, with a yield of 4.5 per cent. These were the best results obtained in any of the experiments reported in Table V.

Table V gives the temperatures or temperature ranges for the catalysts used. Run 275A gave indication of oil formation at 455° C. On repeating the run more carefully a sharp critical temperature of 468° C. was observed. Runs 278A and B both gave a critical temperature of 470° C. Run 280 gave indication of some oil formed between 450° and 490° C. From these observations it is apparent that a critical temperature exists below which the formation of an oily layer is not observed. Before this temperature is reached some higher alcohols may be formed and dissolved in the aqueous layer. The alcohols above propanol, however, are only sparingly soluble in water, although the lower alcohols tend to increase their solubility. The temperatures recorded here were measured with the pyrometer tube inserted in the middle of the contact mass and fall within the range recommended by the patents previously cited.

No attempt was made in these experiments to verify the claim in regard to a critical gas velocity.[6] In general, the pressure and gas flow were kept within the range recommended in the various patents and seem to be far less important than the temperatures which define so sharply the region between methanol formation and higher alcohol formation.

COMPARISON OF RESULTS WITH TWO TYPES OF CATALYSTS

It is interesting to compare the best results obtained with the two types of catalysts (Table VII). On the basis of entering carbon monoxide, 13.9 per cent of useful products were obtained with the oxide catalyst, 10.5 per cent appearing in the oily layer and 3.4 per cent in the aqueous layer. The yield of useful products other than methanol was 11.3 per cent. Of the 16.8 per cent of useful products obtained with the iron-alkali catalyst, 13.4 per cent appeared in the oily layer, and 3.4 per cent in the aqueous layer. Although the iron-alkali catalyst gives a slightly larger yield of useful products in the oily layer, the waste products formed by the reaction are disproportionately higher than with the oxide catalyst.

Another interesting point of comparison lies in the type of product obtained by the two catalysts as shown by the boiling ranges given in Table VII. Although the two give about the same amount boiling below 80° C., a marked divergence occurs above this point. Analyses have already been given showing that the products from the oxide catalyst consist mainly of higher alcohols. Ultimate analyses of the oily products obtained in the two most efficient experiments with a chromium steel–alkali catalyst are shown in Table VIII. The exact nature of the substances obtained with the iron-alkali catalysts has not been determined. In view of Fischer's results, however, the oil is considered as consisting of a mixture of higher alcohols, aldehydes, ketones, and acids, together with some higher hydrocarbons.

Table VII—Comparison of Metallic Oxide Catalyst and Iron-Alkali Catalyst

	Iron-Alkali	Metallic Oxide
	%	%
Entering CO converted to useful products	16.8	13.9
Entering CO converted to waste products	56.7	34.1
Entering Co unconverted	26.5	52.0

Iron-Alkali Catalyst		Metallic Oxide Catalyst	
Boiling range of product	Over	Boiling range of product	Over
° C.	% *by volume*	° C.	% *by volume*
45 to 80	20	45 to 80	23
80 to 117.5	20	80 to 117.5	56
117.5 to 156	20	117.5 to 123	16
156 to 179	20	123 and up	5
179 to 209	10		
Residue	10		

Table VIII—Ultimate Analyses of Products Obtained with Iron-Alkali Catalysts

Run	Carbon	Hydrogen	Oxygen
	%	%	%
168B	54	13	33
217	72	12	16

Conclusions

From a study of these data it is apparent that the portion of carbon monoxide lost in wasteful side reactions is considerable for both iron-alkali and metallic oxide catalysts. While a certain formation of carbon dioxide may be unavoidable owing to the type of reactions involved, there can be no doubt that the high temperature of operation is responsible for a large part of the losses. Thus, it has been noted all through this investigation, as well as in the study of the methanol reaction, that the higher the temperature the greater the tendency for wasteful side reactions to occur. This detrimental feature might be counteracted by the development of more active catalysts which would permit operation at lower temperatures. The side reactions would be further suppressed by employing even higher pressures. From the point of view of losses, the metallic oxide catalysts seem most promising in that they do not possess the marked tend-

ency to form methane, as do the contact substances containing metals of the iron group. Furthermore, the useful products from the oxide catalysts consist mainly, if not wholly, of alcohols, while the iron-alkali catalysts are more uncontrolled in their action, yielding complex mixtures of practically all of the simpler types of oxygenated aliphatic hydrocarbons as well as straight paraffins.

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Phenols in Petroleum Distillates[1]

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THE alkaline solutions used for treating petroleum distillates have been found to contain phenolic compounds which are readily detected by a strong odor resembling cresols when such solutions are neutralized. Although the phenols comprise a very small percentage of most distillates, they may accumulate to the extent that the disposal of waste liquors around refineries may become no small problem. The pollution of small streams or larger bodies of water near city water supplies and the odors arising from caustic wash waters, especially those used in treating cracked distillates, are some of the complaints with which refiners have already been confronted.

A solution to the problem of a means for disposal of such materials is reached in many refineries by one of the following methods:

(1) Neutralization of acid sludge, resulting from acid treatment of distillates, with alkaline phenol-bearing liquors and burning of the neutralized fuel.

(2) Treatment of the alkaline phenol liquors with flue or exhaust engine gases, thereby converting the caustic to sodium carbonate and liberating the phenols, which are then collected and disposed of by burning or some other suitable means.

Phenols have been separated from petroleum distillates and studied. The larger quantity present in cracked distillates shows that the reaction producing these compounds occurs primarily in the cracking process. Results of the investigation indicate that the product is composed chiefly of high-boiling compounds, with very little or no carbolic acid, but the cresols have been isolated and identified. A comparison is made of the petroleum phenols with those from other sources and a resemblance to those from low-temperature carbonization of coal pointed out. Low-boiling cracked distillates may be selected which yield phenols approaching the composition of commercial cresylic acid although the yield is too small to be commercially attractive under normal refinery conditions.

It is apparent that burning has been the simplest and prevalent means of disposing of petroleum phenols. The small quantity available might curtail any elaborate process of recovery and refining; yet in cases where sanitary conditions prohibit dumping into sewage, separation may be necessary and the most economical method of disposal of the recovered product become an important issue. Fuel is relatively cheap, and the use of phenols for this purpose may be regarded as a means of getting rid of an undesirable by-product. A better use will probably be found after the composition and nature of the product is fully understood. For this reason the present investigation was undertaken.

Previous Work

A survey of the literature disclosed that little work had been done on the investigation of petroleum phenols. Other chemists have noted the presence of phenols in cracked distillates, but are not in entire agreement concerning the nature of the compounds. Brooks and Parker[2] state:

The writers have recently examined the oil extracted from cracked gasoline by washing with caustic soda prior to treating with acid, and find that this oil, precipitated from the aqueous alkali by dilute sulfuric acid, consists chiefly of cresols and phenol.

Catlin[3] has published a brief description of cresylic acid separated from caustic soda which had been used in the first stage of a continuous unit treating cracked distillates. Table I shows a 500-cc. distillation in an Engler flask on the product as given by Catlin. He says:

All these fractions reacted positively to the tests for cresylic acid as outlined by Allen.[4] The fractions between 195° and 205° C. and between 205° and 210° C. had a specific gravity of 0.9951 and 1.052 (15°/15° C.), respectively, thus showing the absence of *o*-, *m*-, and *p*-cresols.

Catlin further states:

The relation of specific gravity to the boiling point on the petroleum acid suggests methylphenylcarbinol, (K) $CH_3(C_6H_5)CHOH$, specific gravity 1.003 (25°/25° C.), boiling point 218° to 220° C.

Table I (from Catlin)

(Specific gravity of sample, 1.058)

TEMPERATURE	PER CENT OFF	SPECIFIC GRAVITY OF 10 PER CENT FRACTIONS
101	10 (water)	
195	15 (water and oil)	
205	25	0.9951
210	35	1.0052
212	45	
219	55	
226	65	1.0262
227	75	1.0270
232	82	
	Average (195–227° C.)	1.0134

The conclusion of Catlin that *o*-, *p*-, and *m*-cresols are absent is probably not justified, because the presence of hydrocarbons, either from cracking during distillation or held in solution by the sodium phenolate, may have accounted for the low gravity of the particular fractions. On the other hand, it is very unlikely that the fraction described by Catlin was methylphenylcarbinol, as alcohols of this type should not be extracted by aqueous caustic soda.

Brooks and Parker give no data to substantiate their conclusion that the product extracted from gasoline was chiefly phenol and cresol. The high-boiling character of

[1] Received October 24, 1927.

[2] *Ind. Eng. Chem.*, **16**, 587 (1924).

[3] *Ind. Eng. Chem.*, **18**, 743 (1926).

[4] Allen's Commercial Organic Analysis, 4th ed., Vol. III, p. 316.